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Electrochemical, NMR and FT-IR studies in an ambient temperature chloroaluminate molten salt, consisting of 1-methyl-3-ethylimidazolium chloride, ImCl , mixed with aluminum chloride, are summarized. This work was related to the development of a thermally regenerative fuel cell. Particular emphasis was placed on studies of proton in the molten salt system and physical properties of imidazolium hydrogen dichloride, ImHCl_2 .

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**Electrochemical Studies of Lewis Acid-Base Systems for Use in
Thermally Regenerable Fuel Cells**

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December 31, 1991


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Objectives

Our objective was to study chemistry and electrochemistry in and of Lewis acid-base and mixed Lewis acid-base-Brønsted solvents, which are low temperature molten salt systems. This work was carried out in collaboration with a related, but more application oriented effort, at Hughes Aircraft, El Segundo, California. These solvent systems were proposed for potential use in an electrochemical power source, a thermally regenerable fuel cell (TRFC).

Technical Approach

We utilized an ambient temperature molten salt consisting of 1-methyl-3-ethylimidazolium chloride (ImCl) mixed with aluminum chloride (AlCl_3). This solvent system is characterized as acid, basic, or neutral, if the mole ratio of AlCl_3 to ImCl is greater than, less than, or equal to unity, respectively. Proton was introduced quantitatively by the addition of ImHCl_2 , which is itself an ambient temperature molten salt. The underlying Lewis acidity of the solvent is varied by changing the system acidity; this is accomplished by varying the mole ratio of AlCl_3 to ImCl. Variation in the Lewis acidity then effects the Brønsted acidity of the added proton. A variety of electrochemical, infra-red and nuclear magnetic resonance studies were carried out. Studies to obtain some needed physical properties of the ImHCl_2 itself, which was to be employed by Hughes in their efforts to make a practical device, were carried out.

Results

A Technical Report detailing the determination of the viscosity, conductivity and density of the $\text{ImCl}(\text{HCl})_{1.3}$ molten salt was issued; these properties were measured from 15 to 45 °C.

A number of meetings were held with Hughes Aircraft personnel working on the project to discuss aspects of the program during the period of the contract, and, as a result, a patent application, joint between Hughes Aircraft personnel and the Principal Investigator of this contract, was made.

^2H NMR was employed to obtain information on the nature of the proton in these melts, and to clarify the results of some previous work which had postulated an unknown, but specific form of "acidic" proton. It was shown that, in basic melts, the proton is involved in an equilibrium involving HCl and HCl_2^- , and that only HCl exists in the acidic melt. The constant for the equilibrium between HCl and HCl_2^- was determined by NMR and studied as a function of temperature to obtain enthalpy and entropy data for the reaction. It was also found, by FT-IR studies, that ^2HCl and the "acidic" form of deuteron were not in equilibrium but instead were involved in a kinetic process which consumed

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^2HCl and produced the "acidic" form. Time resolved FT-IR spectroscopy clearly demonstrated that this kinetic process was in fact hydrogen-deuterium exchange where deuterium from ^2HCl exchanged with protium on the H-4,5 position of the imidazolium ring.

Voltammetric studies of the reduction of proton from the melts indicated that, in basic melts, the HCl_2^- species was the electroactive, diffusing species.

In addition, neutron diffraction studies on the ImHCl_2 were carried out at Argonne National Laboratory on a joint project between Dr. David Price, of Argonne, and the Principal Investigator of this contract; this work was supported by Argonne National Laboratory. Although the experiment was successfully carried out, the data, as of this date, has not been completely analyzed.

In work related to, but not funded by ONR, the interaction of proton with organic bases in these molten salts was also investigated. These studies, however, were related to work carried out at Hughes Aircraft

Publications

"Viscosity, Density and Conductivity of $\text{ImCl}(\text{HCl})_{1.3}$ ", Kejiro Sawai and Robert A. Osteryoung, ONR Technical Report No. 1 on Contract N00014-89-K-0056, February, 1990.

*"Lewis and Brønsted Acid Adducts in Ambient Temperature Chloroaluminate Molten Salts", P. C. Trulove, R. T. Carlin and R. A. Osteryoung, *J. Am. Chem. Soc.*, **112**, 4567 (1990).

*"A Mixed Lewis Acid-Brønsted Acid Ambient Temperature Ionic Liquid: An Electrochemical and NMR Study of Dimethylaniline", Soo-Gil Park, Paul C. Trulove, Richard T. Carlin and R. A. Osteryoung, *J. Am. Chem. Soc.*, **112**, 4567 (1990).

*"Interaction of Protons with Solutes in Ambient Temperature Chloroaluminate Molten Salts: Electrochemistry and NMR Spectroscopy of Protonated Anthracene", P. C. Trulove, R. T. Carlin and R. A. Osteryoung, *Proceedings of the Seventh International Symposium on Molten Salts*, C. L. Hussey, S. N. Flengas, J. S. Wilkes and Y. Ito, Eds., The Electrochemical Society, *Proceedings Volume 90-17*, pgs. 306-324, Pennington, NJ (1990).

*"Protons in Ambient Temperature Chloroaluminate Molten Salts: Electrochemistry and NMR Studies of their Interaction with Dimethylaniline", P. C. Trulove, R. T. Carlin and R. A. Osteryoung, *Proceedings of the Seventh International Symposium on Molten Salts*, C. L. Hussey, S. N. Flengas, J. S. Wilkes and Y. Ito, Eds., The Electrochemical Society, *Proceedings Volume 90-17*, pgs. 290-305, Pennington, NJ (1990).

Manuscripts Submitted

*"Electrochemical and Spectroscopic Studies of Anthracene in a Mixed Lewis-Brønsted Acid System", Richard T. Carlin, Paul C. Trulove, and R. A. Osteryoung, *Electrochim. Acta*, submitted for publication.

*"Interaction of 9,10-Anthraquinone with Tetrachloraluminate and Proton in Basic Aluminum Chloride:1-Ethyl-3-Methylimidazolium Chloride Room Temperature Molten Salts", Michael Carter and R. A. Osteryoung, *J. Electrochem. Soc.*, submitted for publication.

* Related to contract work, but not supported by ONR.

** Support by both ONR and AFSOR. Paul Trulove was an Air Force Officer working on his Ph.D. dissertation at SUNY-Buffalo.

Manuscripts in Preparation

"The Nature of Protons in Ambient Temperature Chloroaluminate Ionic Liquids", Paul C. Trulove, K. Sawai, and R. A. Osteryoung, in preparation for Inorg. Chem.

**"NMR Studies of the $\text{HCl}/\text{HCl}_2^-$ Equilibrium in Ambient Temperature Chloroaluminate Ionic Liquids", Paul C. Trulove, D. Sukumaran, and R. A. Osteryoung, in preparation for J. Am. Chem. Soc.

**"H-D Exchange in Ambient Temperature Chloroaluminate Ionic Liquids: Kinetic and Equilibrium Isotope Effects", Paul C. Trulove, D. Sukumarn, and R. A. Osteryoung, in preparation for J. Am. Chem. Soc.

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